COAL PYROLYSIS USING LASER IRRADIATION

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INTRODUCTION

The purpose of this investigation is to observe the effect of laser irradiation on the pyrolysis of coal. Coal irradiated with laser light can decompose into gases rich in acetylene. Coal pyrolysis at the usual coking temperatures yields gases high in methane but very low in acetylene. The acetylene/methane ratio and the probable commercial value of the product gas should be related directly to the temperature of the decomposing coal.

Conventional coal pyrolysis varies in temperature from 450° to 1,400°C and includes hundreds of different processes and coals. A typical high-temperature pyrolysis gas was obtained from a Pittsburgh seam (hvab) coal carbonized at 900° C.[5] Fifteen percent of the coal (40.7 percent volatile matter) was collected as gas (table 1). Laser irradiation can bring about significant changes in the C_2H_2/CH_4 ratio by increasing pyrolysis temperature. The equilibrium constant for the reaction

$$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$$

increases from 10^{-7} at 1,000° K to 10^{+9} at 4,000° K. Temperatures resulting from laser irradiation could be very high. The energy concentration due to a 6-joule focused beam from a ruby laser is sufficient to raise the temperature of a perfect absorber by 14,000° C. This estimate is based on the laser energy and on the heat capacity of the target. However, much of the laser energy is dissipated by reflection, conduction, and vaporization. In these experiments with coal the maximum target temperature was estimated to be less than 1,300° K--largely due to coal volatility. Interesting observations of target temperatures of laser-irradiated solids have been reported. Berkowitz and Chupka[1] analyzed the vapor ejected from graphite and found it compatible with an assumption of thermodynamic equilibrium and a temperature of 4,000° K. Verber and Adelman,[7] using tantalum as a target, measured thermionic emission due to a surface temperature increase which was calculated from classical heat transfer theory. In the following experiments temperatures have not been measured directly due to the small size of the coal crater and to the rapid heating and cooling of the sample.

EXPERIMENTAL

A variety of coals and coal macerals have been exposed to laser irradiation. Using a focused beam, energy concentrations as high as 100 megawatts per square centimeter can be reached. The general procedure has been to seal the coal sample in a glass vessel through which the laser beam can be fired. The vessel was evacuated or evacuated and partially refilled with a specific gas before irradiation. Samples, usually about 8 mm cubes, were sealed in glass tubes 10 mm i.d. and 90 mm long.[6] Samples were dried under vacuum at 100° C for 20 hours, then sealed and irradiated. The usual irradiation was 1 pulse of a 6-joule ruby laser beam which was focused by a convex lens. Gaseous products were analyzed by the mass spectrometer in two or more fractions distilling from liquid nitrogen, dry ice, ice water, room temperature, and 60° C baths. Both total volume and gas distribution were determined for each fraction. Solid products were obtained from the glass walls for ultimate analysis or for inspection by infrared spectrometry.

Table 1.- Product gas

	900°C Carbonization	Laser irradiation
	Mole percent	
H_2	55.6	52.2
CO	7.4	22.5
CO_2	0.4	8.7
CH_4	31.5	5.1
C_2H_2	0.05	10.6
C_2H_4	3.4	0.0
C_2H_6	1.2	0.0
$> C_2$	0.5	0.0
HCN	0.0	0.9
	Weight percent of coal	
	15	52
	C_2H_2/CH_4	
	< 0.002	2.1

In studying any new process for coal pyrolysis, there are several useful variables to be considered. Among these are coal rank, maceral, particle size, and atmosphere. There are also several variables which are characteristic of the processing unit. For the laser they are quantity of energy discharged, rate of discharge, area of target, and wavelength of radiant energy.

Coals have been treated with the same total light energy from 3 different lasers. Lasers used in these experiments were as follows: The ruby laser delivers 6 joules of 6,943 A light in about 1 millisecond. Source of the light is a cylindrical ruby 76 mm long by 6.3 mm in diameter. It is activated by a xenon flash lamp and a capacitor capable of delivering a 2,000-volt pulse. The neodymium laser is a glass rod 152 mm long and capable of a 28-joule pulsed discharge. The third laser type is a continuous CO_2 laser. Its total power output is only 10 watts (10 joules/sec) but since it operates continuously the total energy and the quantity of product gas can be made to equal that of the pulsed lasers. Irradiation from the CO_2 laser has a wavelength of 106,000 A.

RESULTS

A comparison of product gases from a 900° C carbonization and from irradiation by a ruby laser verified the prediction of higher C_2H_2 to CH_4 ratio for the laser (table 1).

Rank. Coal composition and coal utilization vary widely with rank. Irradiation products as a function of rank were studied earlier and the results are summarized in table 2.[3] As rank decreases the yield of gaseous product increases. Yields of acetylene, hydrogen, and HCN reach a maximum for a high-volatile bituminous coal.

Macerals. Macerals from a single coal seam can be separated visually or by specific gravity. They provide information about the origin of a coal and about its coking properties. Maceral separation is a tedious job and well separated samples are usually small.[2] Macerals of Hernshaw (hvab) coal in sufficient quantity for laser pyrolysis were irradiated (table 3). As hydrogen and volatile matter in the maceral increased the product gas increased, and the quality of the product gas (based on C_2H_2/CH_4 ratio) decreased.

Table 2.- Product gases from laser irradiation of coals

	Anthracite	Pocahontas lvb	Pittsburgh hvab	Lignite
	Moles x 10^7			
H_2	13	23	30	21
CO	8	5	12	24
CO_2	4	1	3	10
CH_4	1	1	3	1
C_2H_2	3	4	9	6
HCN	0.3	0.3	1.2	0.7
Total[a]	31	35	60	63

a/ H_2O, N_2, O_2 free.

Table 3.- Gas from laser irradiation of macerals of Hernshaw (hvab) coal

Maceral	H_2, percent[a]	Volatile matter, percent[a]	Product gas Moles x 10^7	C_2H_2/CH_4
Fusinite	3.2	13.4	43	59
Micrinite	4.8	31.4	52	34
Vitrinite	5.4	33.7	90	12
Exinite	6.4	55.4	103	8

a/ See reference 2.

Particle Size. Variation of gas yield with particle size was studied. Samples of Pittsburgh seam coal with particle diameters from 240 μ down to 10 μ (figure 1) were irradiated. For the smaller particles there was a modest decrease in methane and an increase in acetylene. This may indicate less cooling by conduction and higher temperatures.

Types of Lasers. Although laser activity has been produced in many different materials, this study has been carried out using only three--ruby, neodymium, and carbon dioxide. The ruby is a pink crystal of Al_2O_3 with 0.05 weight percent of Cr_2O_3. The chromium ions, excited by the xenon flash lamp, emit a pulse of 6,943 A laser light. The intensity of this pulse can be varied by changing the input to the lamp, by focusing the laser beam, and by Q-switching to shorten the discharge time. The standard irradiation for these experiments was a 6-joule pulse discharged in about 1 millisecond. Without optical alteration this produces a crater 6 mm in diameter (equal to the ruby rod) and an energy concentration at the target of 14 kw cm^{-2}. With a focusing lens this is increased to over 40 kw cm^{-2} and, using an electro-optical Q-switch, to 40 Mw cm^{-2}.

The neodymium laser can deliver a 28-joule pulse of 10,600 A light. Using precise focusing but no Q-switching the light intensity at the target is about 400 kw cm^{-2}.

The CO_2 laser has a continuous output of 10 watts at a wavelength of 106,000 A. Using a focused beam it can produce a flux of 0.2 kw cm^{-2}.

Data from these three lasers, including several variations in the energy intensities of the ruby have been compared at approximately the same total energy output to determine if there are differences in product-gas quantity and distribution.

The CO_2 laser emits the least intense light beam because of its slow rate of emission. The ruby pulses were progressively increased in concentration due to focal variations. This can readily be measured on the coal targets. Craters in the coal irradiated by the defocused ruby laser beam had an average area of 1.3 cm^2. All irradiations with neodymium were focused and the craters averaged 0.02 cm^2. The best focused CO_2-laser beam produced a crater with an area of 0.03 cm^2. The product-gas data are shown as functions of crater area (figure 2). Only the data from irradiations with the CO_2 laser were not consistent with the other data due to its slow heating and cooling rates. The more intense laser beams produced greater quantities of product gas and higher acetylene to methane ratios. In figure 3 crater area was replaced by light flux (kilowatts cm^{-2}) and the CO_2-laser data could be included.

Temperature. Since the same amount of energy was available in each of these tests the temperatures of the craters or of the gas generating sites should be related to energy concentration. An attempt was made to estimate these temperatures from the composition of the gas using gas equilibria data. The chief interest is in the relationship between methane, acetylene, and hydrogen. Equilibrium data to 4,000 K are shown in figure 4.[4]

Gas analyses from various laser irradiations were introduced as shown in the sample calculation using data from irradiation with a neodymium laser.

$$K = \frac{(pC_2H_2)(pH_2)^3}{(pCH_4)^2} = \frac{(.00277)(.00987)^3}{(.000774)^2} = .00444$$

$$\log K = 2.351$$

Assuming the gases to be in equilibrium during their generation, figure 4 gives a temperature of 1,250° K. Temperatures were estimated for other laser irradiations where gas analyses were available (figure 5). Temperatures increase consistently with increase in energy concentration. Since acetylene was not detected in the gases from the CO_2 laser a temperature estimate could not be made. However, a gas analysis was available for product from a 900° C carbonization of coal and a comparison with equilibrium data indicated a temperature of 827° C, in reasonable agreement with the measured temperature.

Variations in types of irradiation cause great changes in gas yield and selectivity. However, most of these changes in the product can be explained on the basis of heat concentration at the target. A greater heat concentration increases gas yield, increases the probable crater temperature, and increases the acetylene to methane ratio. Even data from the CO_2 laser fits into this pattern although the heat concentration is achieved by additional radiation time instead of laser power.

Photochemistry. A fundamental question in the laser irradiation of coal is the possible importance of the wavelength of the energy. Is the laser simply a thermal energy source capable of raising coal to high temperatures or can the monochromatic energy stimulate specific chemical reactions in coal? The usual photochemical reactions take place with wavelengths of 2,000 A to 8,000 A.

The lasers available for this coal study were:

Ruby	6,943 A	- visible spectrum
Neodymium	10,600 A	- infrared
Carbon dioxide	106,000 A	- infrared

At this time it is impossible to measure the photochemical influence of the laser energy because duplicate craters have not been produced by different lasers and the temperature effect is much stronger than the photochemical effect. A first estimate is that the influence is small (compare ruby-focus and neodymium, figure 3) but perhaps using lower energy pulses differences can be detected.

Another conclusion to be drawn from these data is the effectiveness of a concentrated beam of laser light in promoting acetylene production in coal pyrolysis. This has been shown for both ruby and neodymium lasers and for coals of varying rank, maceral, and particle size. Due to coal volatility temperatures have been lower than expected. Higher coal temperatures could be predicted by irradiating pretreated coal in a pressurized system and should lead to gas compositions even richer in acetylene.

References

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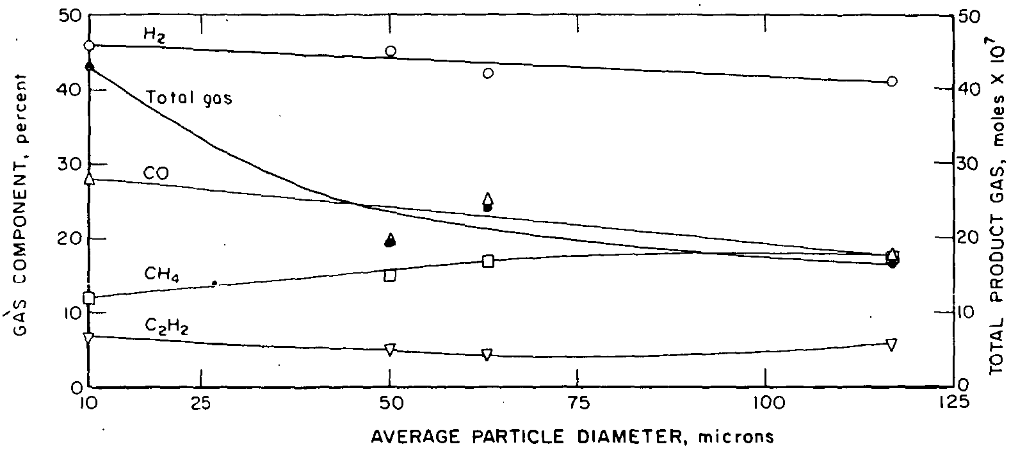

Figure 1. — Laser irradiation of Pittsburgh coal. Product gas as a function of coal particle diameter.

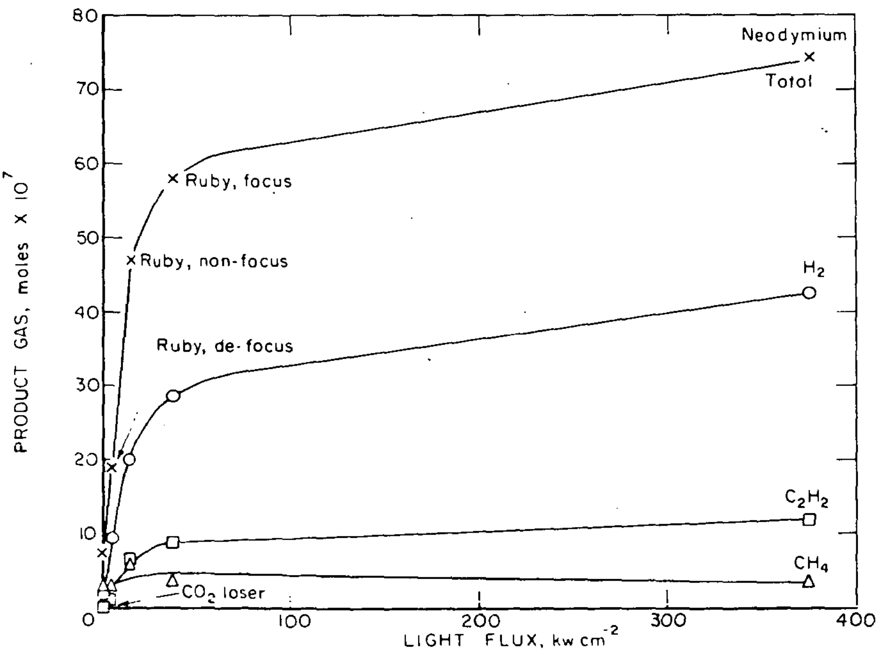

Figure 3 — Gas composition as a function of light flux. Laser irradiation of Pittsburgh seam coal.

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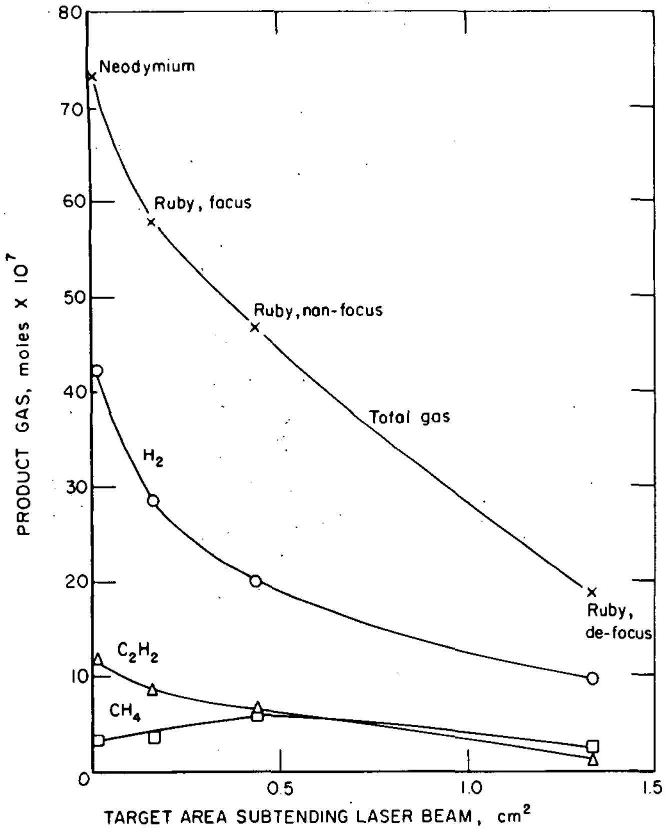

Figure 2.- Pittsburgh seam (hvab) coal irradiated with ruby and neodymium lasers. Gas in moles x10^7 per 6 joule pulse.

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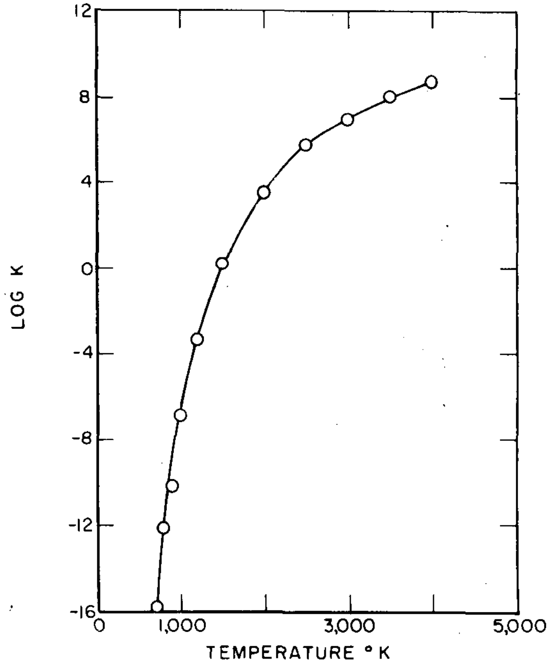

Figure 4.—Equilibrium for $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$ calculated from NASA SP—3001. (ref 4)

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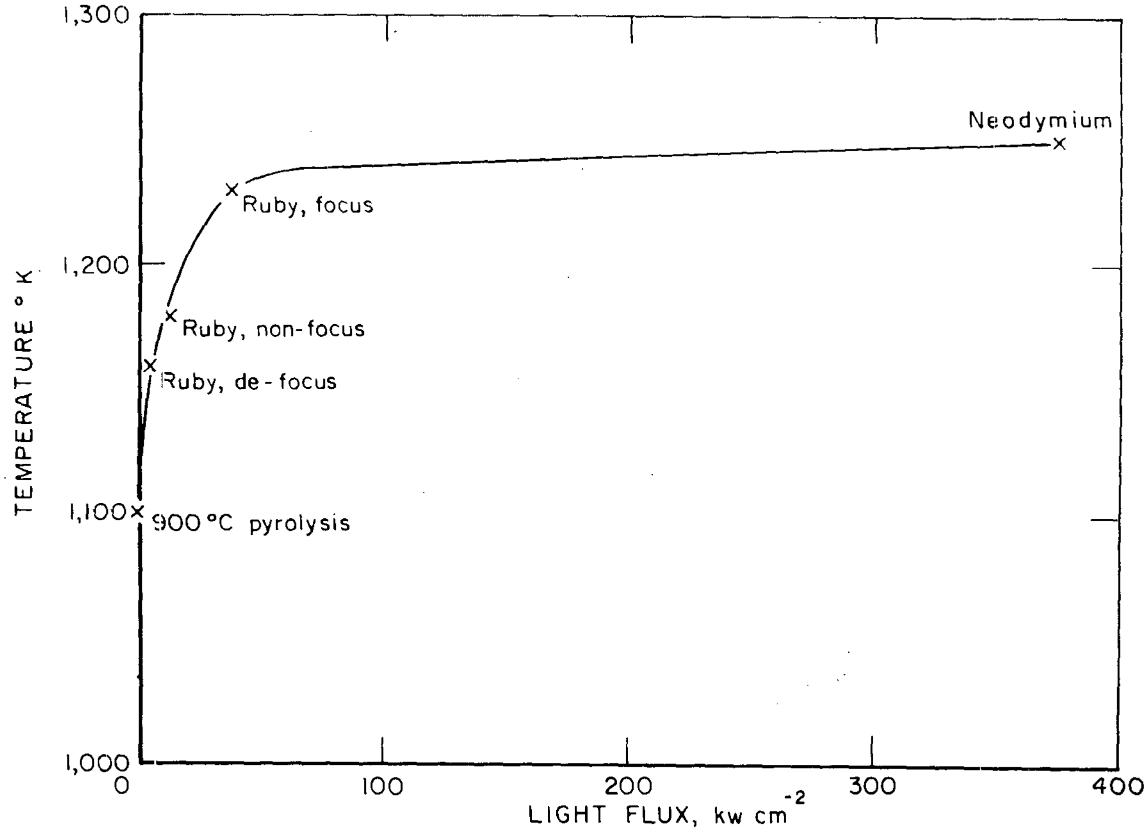

Figure 5.— Temperatures of laser irradiated coal as estimated from gas analyses.

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